DESIGN AND DEVELOPMENT OF AN ELECTRONIC X-RAY PROBE FOR THE STUDY OF ALLOYS AND OF THE STRUCTURE OF METALS

by

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INTERIM TECHNICAL REPORT NO. 1

under

DEPARTMENT of the ARMY
Contract DA-04-495-Ord-463
D/A Project No. 593-08-024
Ord. Project No. TB4-161A

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PASADENA, CALIFORNIA

February 1954

SUMMARY SHEET

FROM: California Institute of Technology
1201 East California Street
Pasadena 4, California

CONTRACT NUMBER: DA-04-495-ORD-463

D/A Project No. 593-08-024

Ordnance Project No. TB4-161A

TITLE: Design and Development of an Electronic X-Ray Probe for the Study of Alloys and of the Structure of Metals.

Report No. WAL 142/59

Interim Technical Report No. 1

DATE: 7 January 1954

Work is being performed under Technical Supervision of Watertown Arsenal Laboratory

TO: District Chief, Los Angeles Ordnance District
35 North Raymond Avenue
Pasadena 1, California

OBJECT: Design and build an instrument in order to obtain an excessively finely focused electron beam which strikes the appropriately prepared surface of the alloy or metal to be studied in a spot whose dimensions are of the order of 10^{-4} cm and to resolve and measure the intensities of the emitted characteristic X-Rays.

AUTHORS: Jesse W. M. DuMond, Pol Duwez, David B. Wittry

SUMMARY SHEET (Continued)

ABSTRACT: Progress on the design and development of an electronic x-ray microprobe for quantitative and qualitative composition measurements of about 1 cubic micron of the surface of metals and alloys is described in this report. The principle is that first used by Castaing, in which the metal is subjected to bombardment by a finely focused probe of electrons and the elements present and their proportions are determined by an analysis of the frequency and intensity of the characteristic x-rays emitted. With the first model of the instrument, it will be possible to study the elements in the ranges of atomic numbers 19 through 34 and 50 through 84. This report omits any theoretical treatment of the effects of heat generated in the sample, fluorescence radiation, or a detailed discussion of the corrections that must be made. These matters will be considered in a later report.

Introduction

An electronic x-ray microprobe which could give accurate composition measurements of the surface of metals and alloys would be an extremely useful tool for investigations in solid state physics and physical metallurgy. Such an instrument, first developed by R. Castaing in France, uses an electron probe focused to about 1 micron in diameter to bombard the surface of the sample.[1] Elements present in the surface of the sample are recognized by their characteristic x-radiation and a determination of the amount present is possible because the ratio of intensity of an x-ray line from a heterogeneous sample to the intensity from a pure metal approximates very closely the concentration of the element in the sample. The approximation depends on the fact that the electron stopping power of equal masses of two different elements is very nearly the same. Obviously a correction can be made to the first approximation, taking account of the differences in absorbing power of different elements for electrons of a given energy. Corrections are also necessary for the self-absorption of the x-rays in the sample, since the electron beam penetrates a finite distance into the sample (for the accelerating voltages used, this is about 1 micron).

In this way, it is possible to make a point-to-point analysis of a metal or alloy, obtaining the composition of about one cubic micron of the surface to an accuracy of about 1% and in a manner that does not involve arbitrary standards and does not require the destruction of the sample. It is not necessary to emphasize the usefulness of such a

method of analysis. Obvious applications are to the study of crystal structures, diffusion in solids, the investigation of semiconductors, and the study of inclusions and grain boundaries in metals and alloys.

The subject of this contract is the development of an electronic x-ray microprobe operating on the same principle as Castaing's instrument, but incorporating a number of changes and modifications. The most important of these is the substitution of a field emission point for a hot cathode as a source of electrons in the probe. This would permit the use of a single electron lens of a low power, since the source of electrons, the field emission point is already of the order of the size of the desired focal spot. In addition to greater simplicity, this would allow more room for inserting optical devices for looking at the surface that is being explored. Large currents can be drawn from field emission points, the problems being (1) to stabilize the current emitted into the electron lens and (2) to reduce spherical aberrations in the electron lens so that a large aperture can be used.

Another change which may prove fruitful would be the substitution of a scintillation counter of a photoconductive crystal detector (such as cadmium sulfide) for the geiger counter as a detector for the radiation.

The low intensities of x-radiation due to the limited area of the sample bombarded and the relatively long wavelengths of the characteristic radiation from the lighter elements make the use of a vacuum x-ray spectrometer desirable so that the attenuation due to air can be reduced. This complicates the spectrometer design somewhat, but it

eliminates the need for a window between the spectrometer and the sample chamber.

The stage which supports the sample in the Caltech version of the instrument will provide for a rotation of the sample about the axis of the electron beam. This will be extremely useful in aligning the focal spot of the probe with the focal circle of the curved-crystal spectrometer, a problem of considerable importance because of the small size of the focal spot. It will also effect a change in the angle of emergence of the x-rays from the sample, giving more information for an accurate correction for self-absorption of x-rays in the sample.

A final improvement which it is proposed to try is an arrangement of two curved crystal spectrometers which could measure intensities of two different lines simultaneously. This would be one way of overcoming the difficulty of an unstable beam current as well as providing more convenience in making diffusion studies.

During the first year, the project was without active financial support and the progress was very slow. The groundwork of the design of the instrument was accomplished during this period, but most of the equipment was borrowed and had to be replaced with permanent components at the start of the ORD contract on July 1, 1953.

During the first six months of the contract, the personnel working on the project included David Wittry, a graduate research assistant, William Dibble, an undergraduate student, Elmer Smith, a half-time technician, and Ernest Keil, a part-time machinist.

The design work up to the present time consists of about 70 working drawings and covers virtually all of the instrument. Almost all of the parts are completed or are under construction. The first phase of the project is to secure an electron probe with the desired qualities of maximum beam current and minimum size of the focal spot, with either a stable current or provision for taking account of its variations.

Figure 1 shows a general view of the instrument in its present state of development. The cathode assembly, electron lens, sample housing and airlock mechanism are shown in the position for testing, but not in the position they will occupy in the final instrument. The electronic components occupy the rack to the far right as they will in the completed model. The dummy stage which will be used for testing the focal properties of the lens can be seen on the left corner of the table. The microscope and eyepiece camera which will be incorporated in the instrument to give a visual indication of the area being explored is shown resting on the table. This serves to give an idea of the size of the table on which the instrument is being constructed.

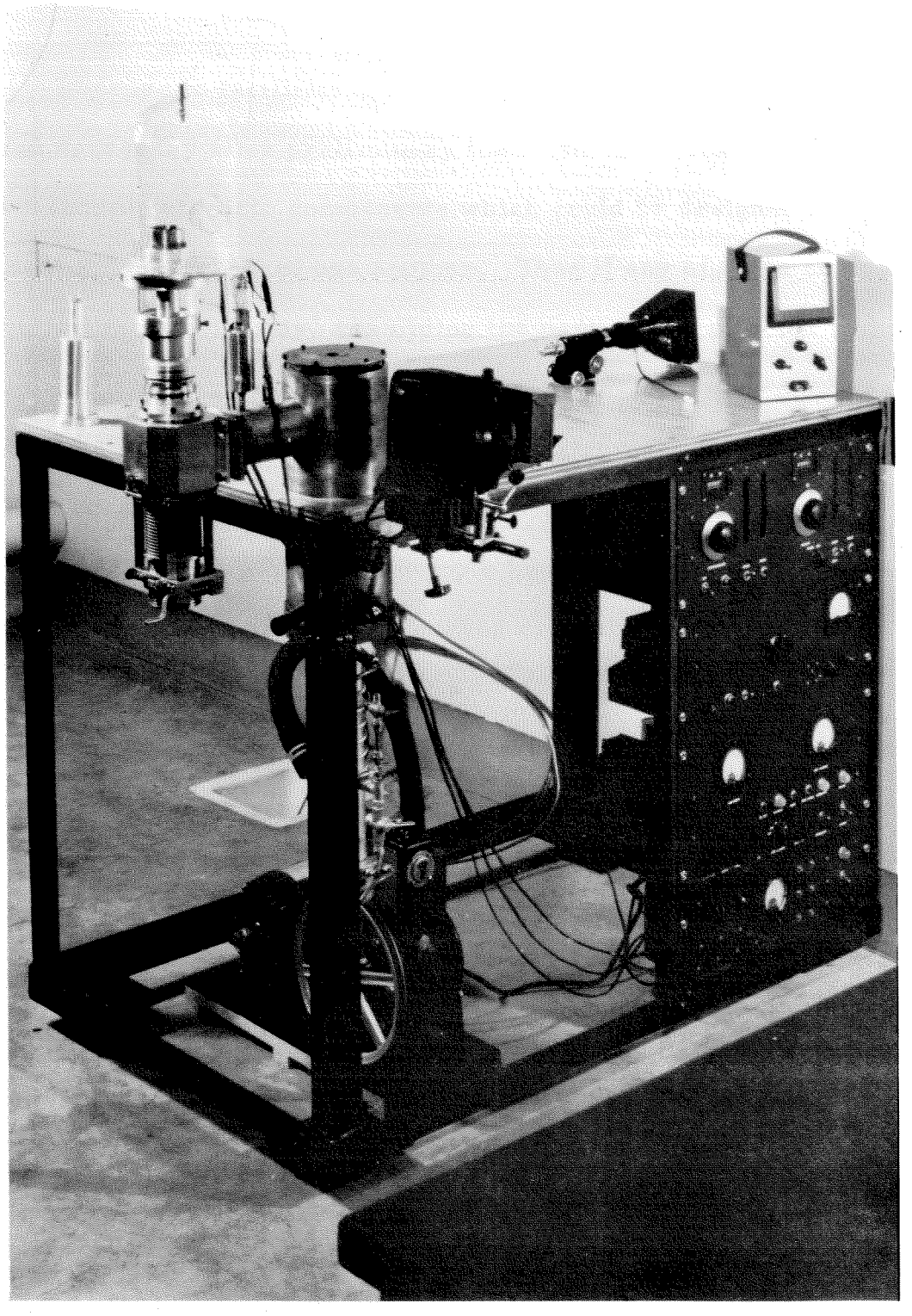

FIG. 1 ARRANGEMENT FOR PRELIMINARY TESTING OF THE FIELD EMISSION CATHODE, ELECTRON LENS AND AIRLOCK

General Design Considerations

In order to facilitate modifications in the design which might be found necessary after preliminary tests, the instrument was broken down functionally into components which could be designed and built almost independently of one another. Thus if any of these components requires major changes, rebuilding the part can be effected without requiring changes in other parts.

The functional components of the instrument are as follows: (1) the vacuum system, (2) the field emission cathode assembly, (3) the electrostatic lens, (4) the sample housing and viewing system, (5) the stage assembly, (6) the curved crystal spectrometer, and (7) the high voltage power supply.

Figure 2 shows a diagrammatic representation of these components, omitting for simplicity the sample viewing system and the vacuum system.

Figure 3 shows the various components arranged as they will be in the completed form of the instrument as it is now contemplated. Because of the possibility of making improvements in the design, this should be regarded only as a tentative idea of the general appearance of the completed instrument.

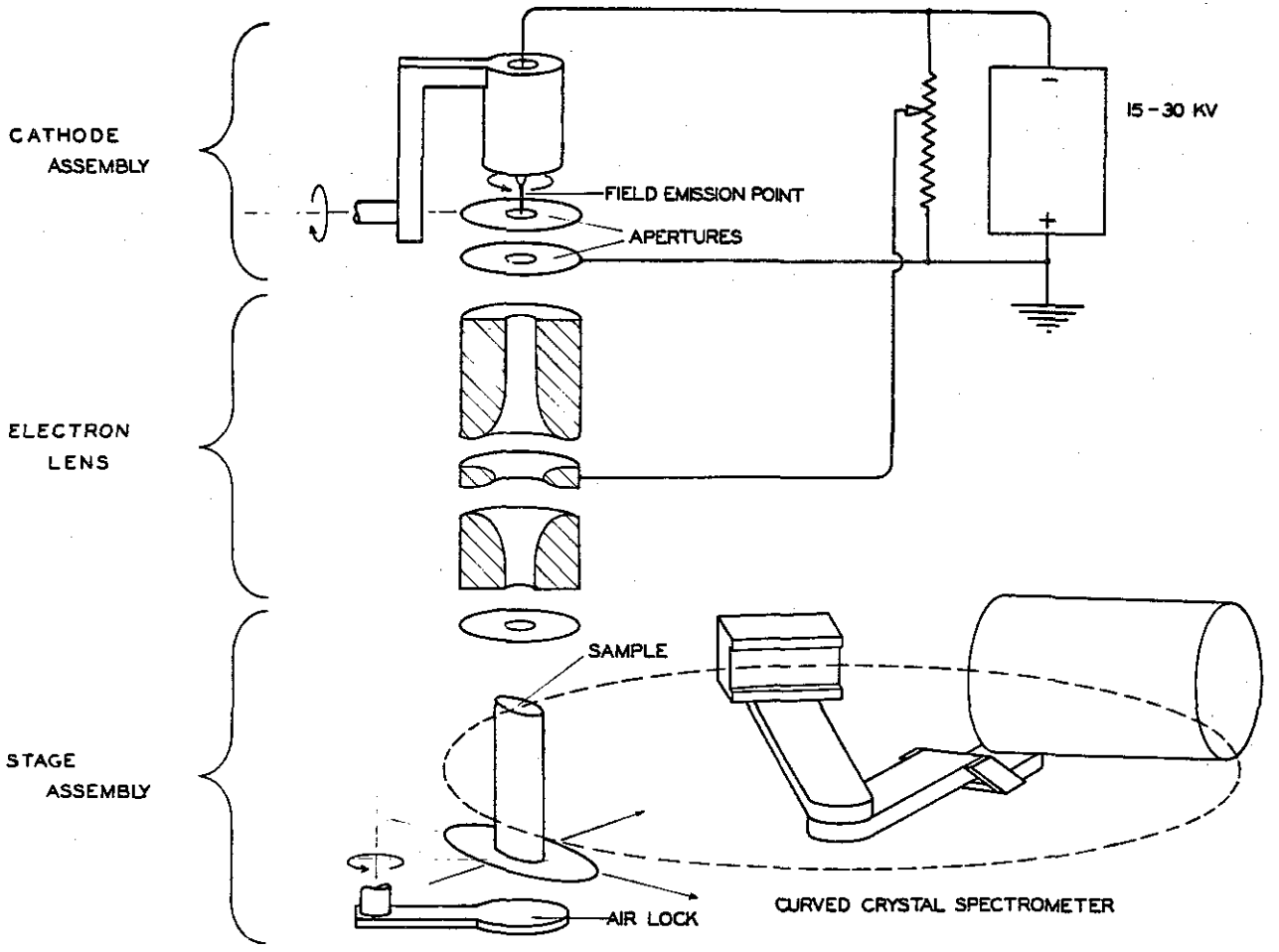

FIG. 2. SCHEMATIC OF THE ELECTRONIC X-RAY MICROPROBE

Key to Figure 3

1. Forepump
2. Data Table
3. Diffusion Pump
4. High Voltage Power Supply
5. Ribbon Filament Illuminator
6. Main Cold Trap
7. Vacuum Gauges
8. Cathode Assembly Cold Trap
9. Cathode Assembly
10. Electron Lens
11. Spectrometer
12. Microscope and Eyepiece Camera
13. Double Scaler
14. Geiger Tube Power Supply and Cycle Timer
15. Ion Gauge Circuit
16. Pirani Gauge Circuits

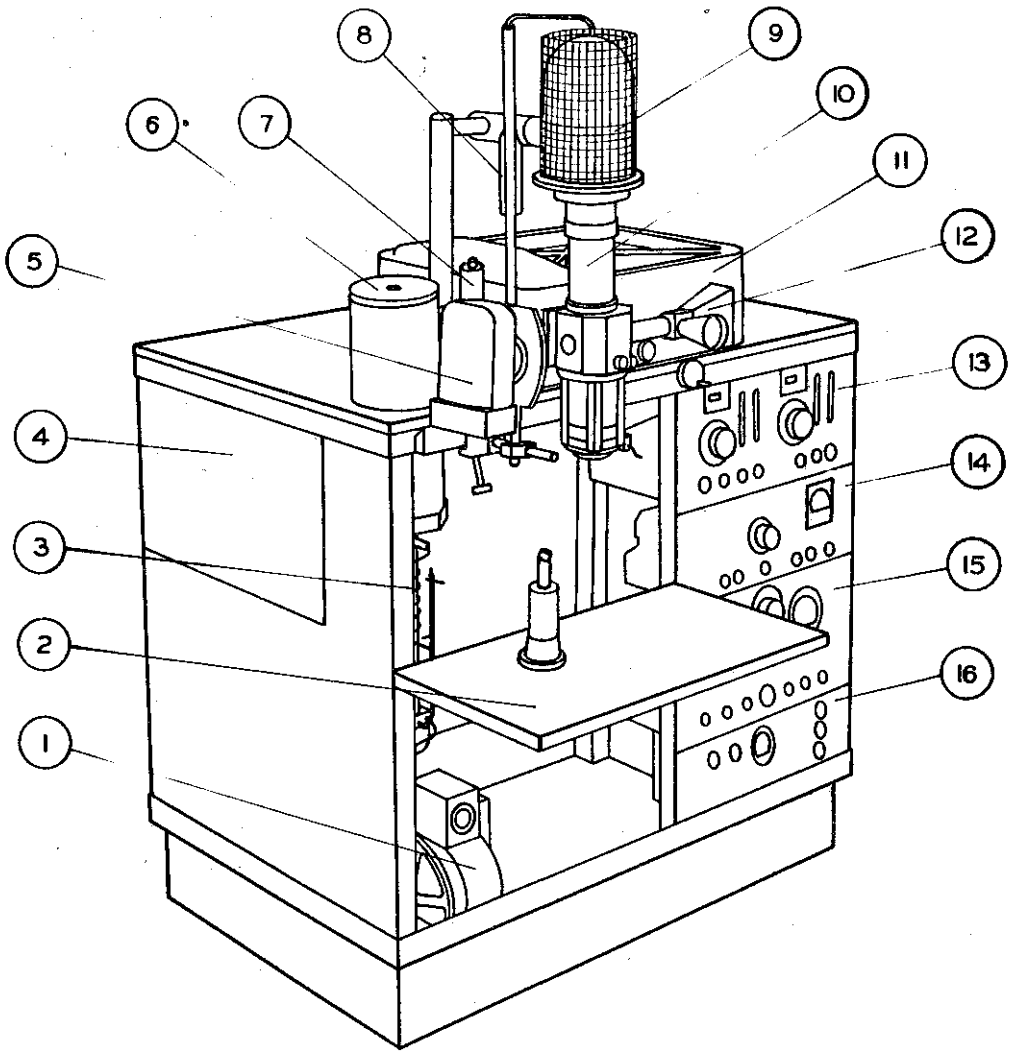

FIG. 3. PRESENT DESIGN OF THE COMPLETED INSTRUMENT

The Vacuum System

The vacuum system consists of a National Research Type H-2 P purifying diffusion pump backed by a Welsch Duoseal No. 1405 mechanical pump. The speed of this combination is about 70 liters per second at a pressure of 10^{-5} mm. An internal cold trap was constructed to which the diffusion pump is attached with a lead gasket. The design of this trap is such as to provide a large conductance to make maximum use of the pumping speed of the diffusion pump. An ion gauge and a pirani gauge are attached to the pumping lead on the side of the cold trap as shown in Figure 4. While a Phillips type vacuum gauge would cover the range of pressures in the major portion of the system, it was thought advisable to use an ion gauge because of the possible necessity of having a differential pumping system in which the cathode is maintained at a much lower pressure than the electron lens or the spectrometer. The reasons for this will become apparent later when the field emission cathode is discussed.

The cold trap was designed in such a way as to bolt directly to the side of the spectrometer box with an "O" ring gasket. For the purpose of testing the lens and cathode before the spectrometer is finished, the stage housing was designed so that it could also be attached to the cold trap.

The pirani gauges were made from 7.5 watt light bulbs by drilling a small hole in the top of the bulb and connecting them to the system by a small "O" ring. The brass cylinder visible in Figure 4 directly

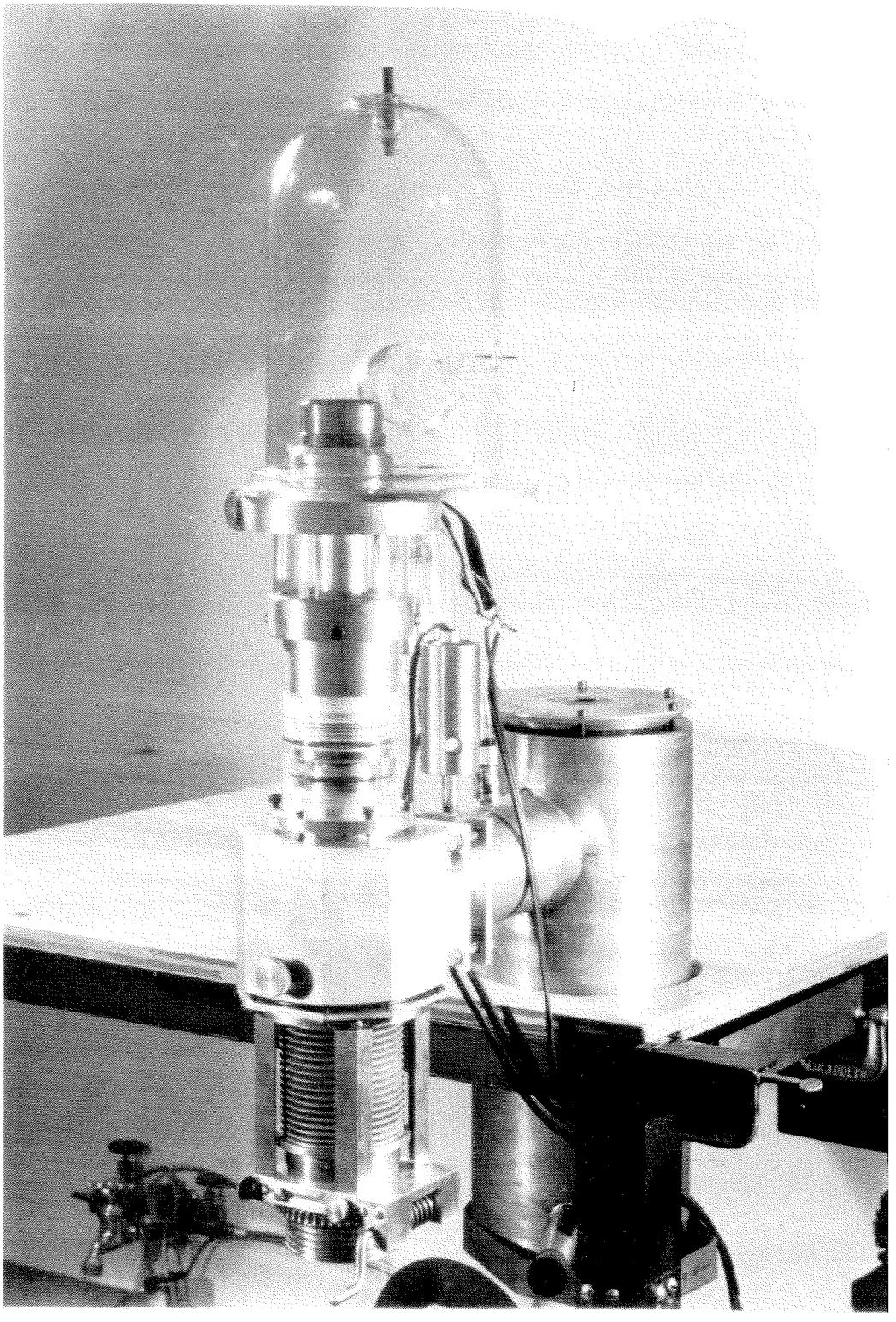

FIG. 4 DETAIL OF THE BEAM FORMING PART OF THE MICROPROBE

above the side tube on the cold trap houses one of these pirani tubes.

The Field Emission Cathode Assembly

Tungsten points suitable for field emission sources can be made by etching wire either in hot fused sodium nitrite or by passing an alternating current between the wire and another electrode emersed in a solution of sodium hydroxide. The electrolytic method is preferable because it is easier to control the size of the point obtained. Well-rounded points with a radius of curvature at the tip of a fraction of a micron can be made in this way. When an electric field is applied between the point and an electrode surrounding it, the small physical size of the point results in a high field density at the surface of the point which draws electrons in large quantities out of the metal. In an ONR report on Field Emission, Dyke and Trolan give direct current vs. voltage graphs for field emission points.[2] Currents in excess of 10^{-6} amps are easily attained with moderate accelerating voltages. (The beam current in Castaing's microprobe was of the order of 10^{-8} amps.)

There are two important considerations in the design of a successful field emission cathode. The primary consideration is the fact that at pressures higher than 10^{-8} mm Hg the emission has a tendency to become unstable, presumably due to the bombarding of the point by positive ions. There are several ways in which this might be reduced. Deflecting magnets could be arranged so that the returning positive ions

would not impinge on the point. This method, however, might introduce serious aberrations in the lens system, as from an off-axis source for example. The lines of attack which will be tried in the Caltech program are (1) differential pumping to maintain the cathode at low pressure and (2) choice of the emitter and aperture geometries so that the positive ions do not strike the emitter tip. (According to Professor Dyke, this is possible because the positive ions, being heavier than the electrons, do not exactly follow the field lines, but are deflected less, and can thus be made to strike parts less sensitive to changes in geometry than the emitter tip.) A final possibility which can be resorted to if the other methods fail is the use of pulsed accelerating voltages.

The second consideration in the design of a field emission cathode is the intensity distribution of the electrons emanating from the point. The tip of the point is approximately hemispherical in shape, but the emission is not the same in all directions; instead it is characteristic of the crystal structure of the tungsten. It is very desirable to be able to orient the point in such a way as to permit the areas of low work function and, therefore, high emission to contribute the electrons which are accepted by the aperture stop preceding the electron lens. The cathode holder is, therefore, designed in such a way as to permit a rotation of the tungsten wire about its own axis and a rotation about an axis perpendicular to the wire and passing through the point. These adjustments are made by shafts passing down the

pumping lead through a baffle in a second cold trap so that there will be no "O" rings in the high vacuum portion of the cathode assembly. These parts are not illustrated in any of the figures as some of them are still under construction.

The aperture which limits the solid angle of electrons in the beam is adjustable from outside the vacuum system so that its distance from the emitter can be changed. This varies the solid angle subtended by the aperture at the point and consequently the beam current. The desired setting is one in which there is a compromise between maximum current and minimum size of the focal spot as limited by the spherical aberration of the lens.

Glass to metal seals will be made with a thermosetting plastic "Araldite" manufactured by CIBA Limited, Switzerland and when the initial difficulties have been overcome, it is planned to seal the glass bell housing the cathode to the aluminum plate which supports it. The change of emitter points will then be accomplished through removal of the apertures from below. The taper plug assembly holding the point previously aligned in a jig is replaced through the opening from which the apertures were removed. This arrangement placed the "O" ring which joins the cathode assembly to the electron lens on the low vacuum side of the aperture. This "O" ring provides for a transverse adjustment of the cathode assembly relative to the electron lens. The design allows for baking out of the cathode assembly at low temperatures and the point itself is to be mounted as in Dyke and Trolan's work on a tungsten hairpin filament which can be used to outgas the point.

The Electrostatic Lens

It was decided to use electrostatic focusing of the electron beam because the problems of stabilizing the voltages are less than with magnetic lenses. Electrostatic lenses which are supplied with voltages in phase with the accelerating voltage are relatively insensitive to fluctuations in voltage provided the velocities of the electrons are not relativistic.

In a beam-forming device, where the object is to get the greatest intensity into the smallest possible focal spot, the spherical aberration of the electron lens system is the most important lens effect. Accordingly, the electrodes of the electrostatic lens were patterned after plots made by Plass[3] of the equipotential distribution giving the axial distribution:

$$V(z) = V_o + A \exp(-Bz^2)$$

O. Sherzer[4] has shown that an axial potential of this form will give an electron lens of minimum spherical aberration.

The central element of the lens is of stainless steel and has an aperture of 1/2 inch (the electron beam will not make use of this entire aperture). The outer electrodes, which will be at ground potential (positive with respect to the central aperture and the cathode) are symmetric and are made of aluminum for ease in machining. In machining these electrodes, the coordinates of the curves were entered directly on the lathe and the steps then smoothed out. The machining of the surfaces is probably accurate to the same degree that the coordinates could be determined from Plass's graphs.

The insulator in the lens is lucite which is machined in such a way as to position the electrodes. The "O" rings are located so as to minimize the effects of changes in dimensions of the lucite which is exposed to vacuum. Figure 5 shows an exploded view of the electron lens, illustrating the shape of the electrodes and the method of assembly.

The Sample Housing and Viewing System

When the sample is in position for making an analysis it is enclosed in an octagonal aluminum block shown in Figure 6. This block is attached to the electron lens with an "O" ring and seals to the spectrometer with a sliding "O" ring. It will be bolted to a sub-base which slides on ways attached to the side of the spectrometer box. This arrangement permits the focal spot of the electron beam to be adjusted so as to coincide with the focal circle of the curved crystal spectrometer. The electron lens, sample housing and airlock mechanism can thus be removed from the spectrometer without affecting this adjustment. When the sample is lowered by means of a sylphon, the gate valve shown in Figure 6 can be closed so that the sample can be changed without opening the rest of the system to air.

It is necessary to have a visual indication of the area of the metallic surface being analyzed. This will be accomplished by means of an optical microscope which should have a resolving power of the same order as the size of the focal spot, i.e., 1 micron. There are several difficulties in attaining a good optical system. The eyepiece cannot be along a perpendicular to the surface because of the close

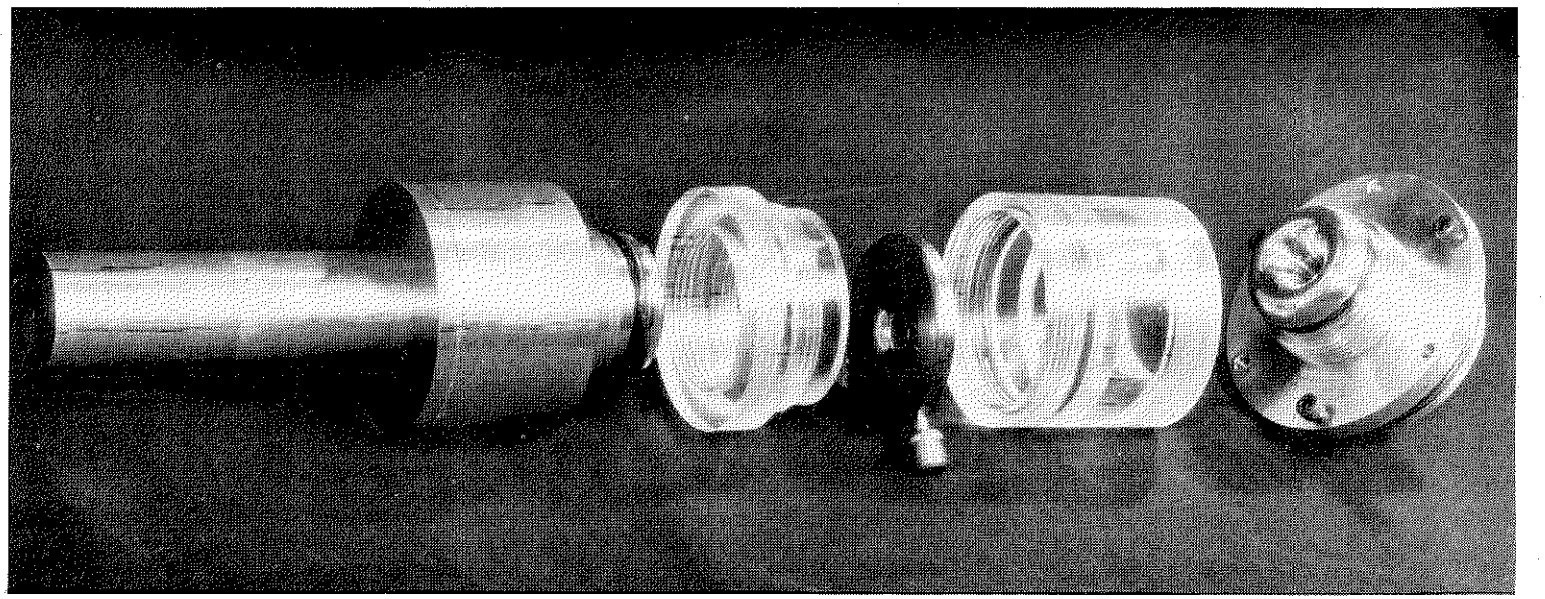

FIG. 5 EXPLODED VIEW OF THE ELECTRON LENS, SHOWING THE SHAPE OF THE ELECTRODES AND METHOD OF ASSEMBLY

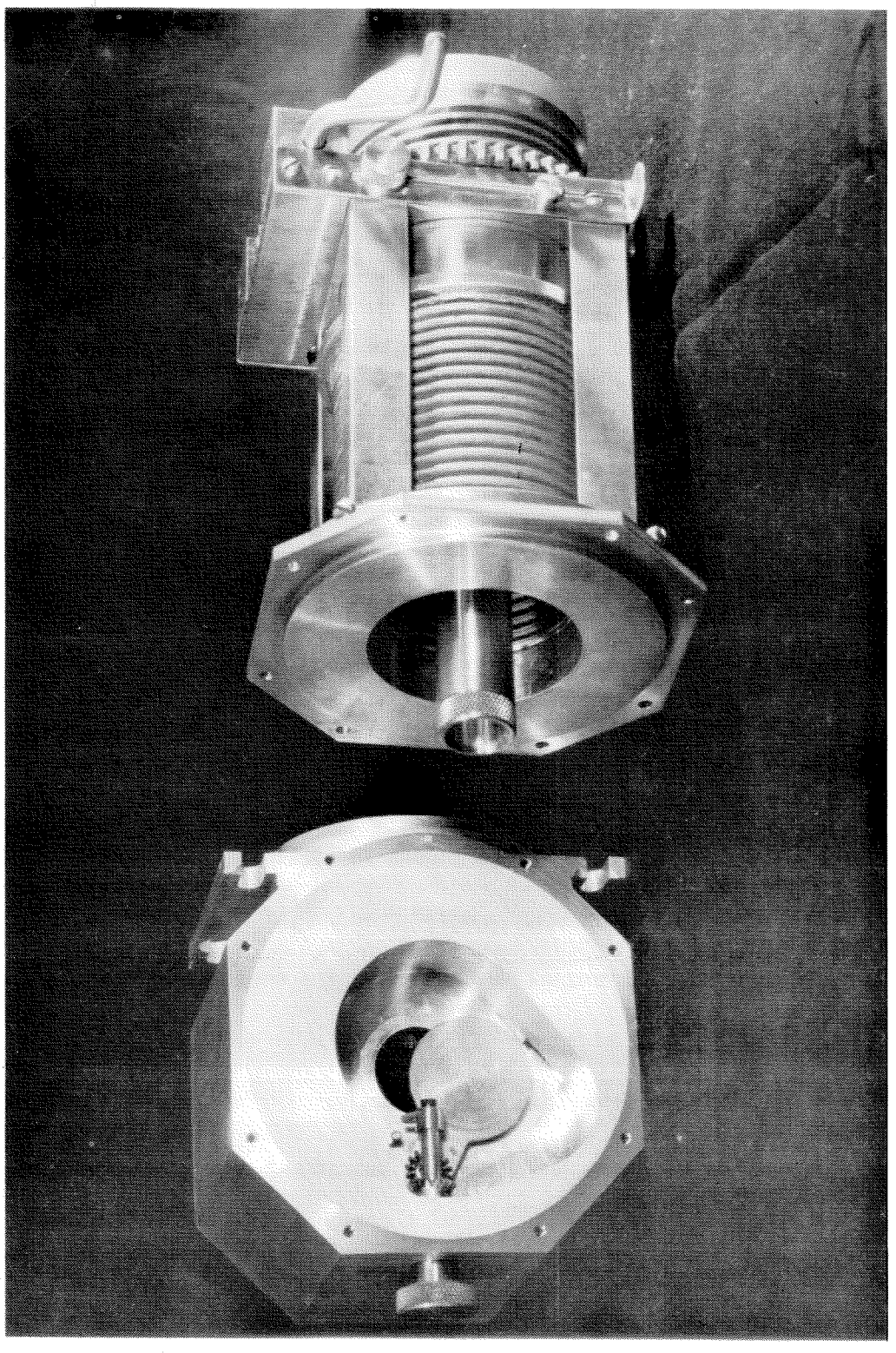

FIG. 6 THE AIRLOCK GATE VALVE AND STAGE HOUSING

proximity of the electron lens, the numerical aperture of the objective and the mode of illumination must be such that the desired resolving power can be obtained, and the electron beam must pass through the optical parts above the sample unhindered.

Two systems are being studied in order to find the most satisfactory. The first system uses a combination of an aspheric mirror, or a lens mirror and a half silvered mirror to transfer the image to a point where it can be conveniently examined with a conventional objective.[5] The second system is the familiar Schwarzchild reflecting objective using a combination of concave and convex mirrors.[6] The Schwarzchild system unfortunately removes light in the central part of the system which may affect the resolving power in an unpredictable manner. In general the effect of an obstruction in the center of a circular aperture is to reduce the intensity in the Airy disk with an increase in the intensity of the first ring in the diffraction pattern.[7] For a specimen of high contrast the resolving power may be increased since there is also a slight decrease in the diameter of Airy's disk, but for a specimen of low contrast, there is a decrease in the resolving power.

The viewing system will also serve to position the sample in a vertical direction, the sample being in the correct position when it is in focus. Cross hairs in the eyepiece will indicate the point of the sample that is directly under the electron beam. An eyepiece camera will be used to photograph the area that is being analyzed. The table

on which the instrument is mounted is such that the viewing screen of the eyepiece camera comes approximately at eye level (see Figure 3).

The Stage Assembly

The stage has been designed so that the sample is inclined at 15^{o} to the horizontal. The spectrometer is in a horizontal plane and the electron beam perpendicular to this plane. The x-rays accepted by the spectrometer, therefore, leave the sample at an angle of 15^{o} with its surface in order to reduce self-absorption in the sample.

The sample can be translated in the plane of its surface in two perpendicular directions a distance of 2 mm. An area of 4 square millimeters can thus be explored. The motion of the sample is accomplished by two precision screws on the base of the plug-like assembly which can be removed in its entirety to change samples. These screws move blades with wedge-like faces which translate the sample. The nobs attached to the precision screws are to be calibrated in microns with 50 microns per revolution.

The stage can be rotated about the taper which positions it in the part attached to the sylphon. This part is threaded and permits raising and lowering of the sample by means of a worm gear (see Fig. 4). Provision is made for adjusting the axis of this taper so that it can be made to coincide with the electron beam. In changing field emission points, the axis of this taper indicates the adjustments to be made to re-align the cathode assembly so that the electron focal spot will again be on the focal circle of the spectrometer.

Parts of the stage assembly are still under construction, so a dummy stage, with provision for placing photographic film in place of the sample has been made for the purpose of testing the electron lens. This is the dummy stage shown on the left corner of the table in Fig. 1.

The Curved Crystal Spectrometer

The spectrometer which will be used to analyze the characteristic radiation emitted by the part of the sample under the probe is of the Johann-DuMond type. This type of spectrometer is extremely well adapted for this application because of the small size of the source of x-rays and because the focusing action helps to compensate for the low intensity of radiation.

The crystals for the spectrometer, loaned by the Physics 15 group of Caltech, were purchased by Dr. Jesse W. M. DuMond in France from Jobin and Yvon, 26 rue Buthollet, Arceuil (Seine), France and are ground to a radius of curvature of about 50 cm. They have a grating constant of 3.34 $\mathring{A}$ and measure 3.5 cm by 1.43 cm. The crystal planes made an angle of 3^{o} with the surface of the lamina at its mid point, and this is taken advantage of to give the most space about the sample. With these crystals, it will be possible to study elements of atomic number 19 (Potassium) through 34 (Selenium) by means of their K radiation and atomic number 50 (Tin) through 84 (Polonium) by means of their L radiation.

The spectrometer, as well as the cast aluminum housing, is under construction at present. Some of the completed parts, the

crystal and detector holder, are shown in Figure 7. The setting for various Bragg angles will be accomplished by a single shaft driving two gears in such a way that the Bragg conditions are always satisfied. A calibrated drum on this shaft will be located below the table on which the spectrometer is mounted, where it can be viewed by an observer seated at the data table on the front of the instrument (see Fig. 3).

It is contemplated to try the use of cadmium sulfide crystals as a detector of the radiation. This would permit a large simplification in the electronic equipment since the current which passes through these photoconductive crystals is directly related to the intensity of the radiation.[8] The design also provides for mounting a commercial end-window geiger tube Radiation Counter Laboratories TGC 3 and preventing its mica window from exploding in the vacuum system by a suitable arrangement of the same slit that limits the sensitive area of the counter to a line. This slit will be somewhat larger than necessary to determine the resolution of x-ray lines, the small source of x-rays serving this function.

A combination geiger tube power supply and cycle timer was built which provides independent regulation of the voltage for two geiger tubes. This is illustrated in Figure 8. The cycle timer controls the gate in the doube scaler and provides for readings over a period of up to about 2-1/2 minutes. For use with the geiger counter, a double scaler has been constructed, having two channels with electronic scales of 100 or a single channel with a scale of 10,000.

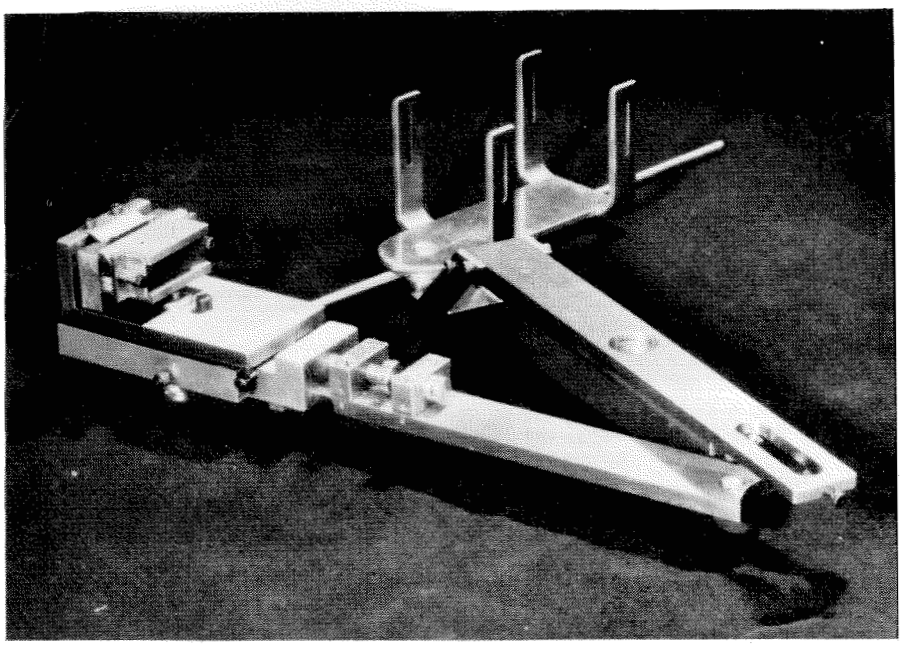

Fig. 7. Completed parts of the spectrometer; the crystal and detector holders.

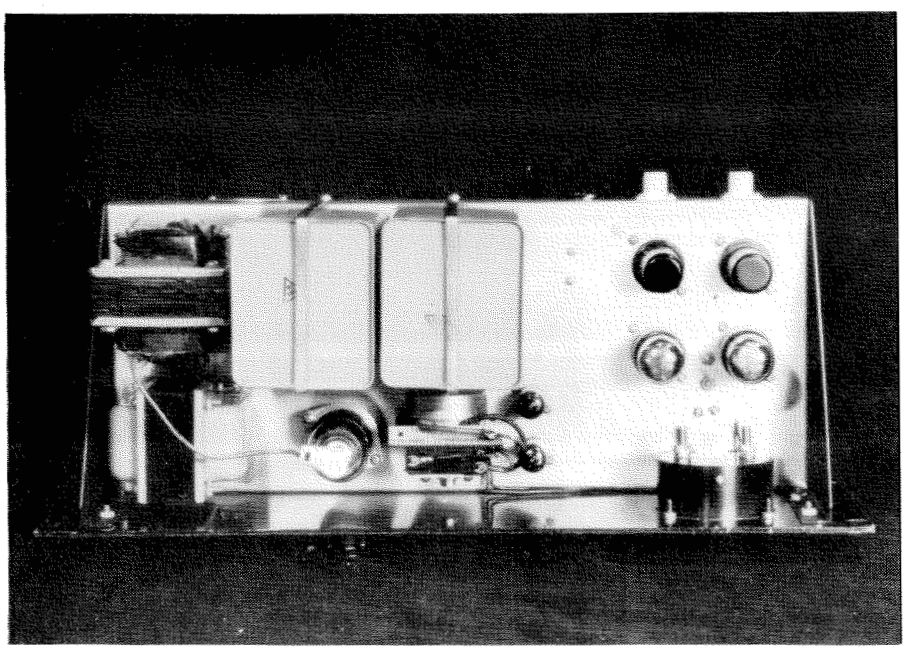

Fig. 8. Top view of the Geiger tube power supply and cycle timer.

The second channel can be used to monitor the beam current, or in the event that a double spectrometer is built, can be used on the second spectrometer. Figure 9 shows a rear view of the double scaler, and Figure 10 a view of the underside of the chassis.

High Voltage Power Supply

For the preliminary tests of the instrument, a power supply which was borrowed from the Electrical Engineering Department of Caltech will be used. It delivers a rectified voltage of 30-0-30 kilovolts by means of a 30 kv oil-insulated transformer in a voltage doubling circuit. The power supply will probably be used for this purpose as a half-wave rectified supply with a resistance-capacitance filter. A regulated power supply, possibly of the RF type, will eventually be substituted as a permanent part of the instrument.

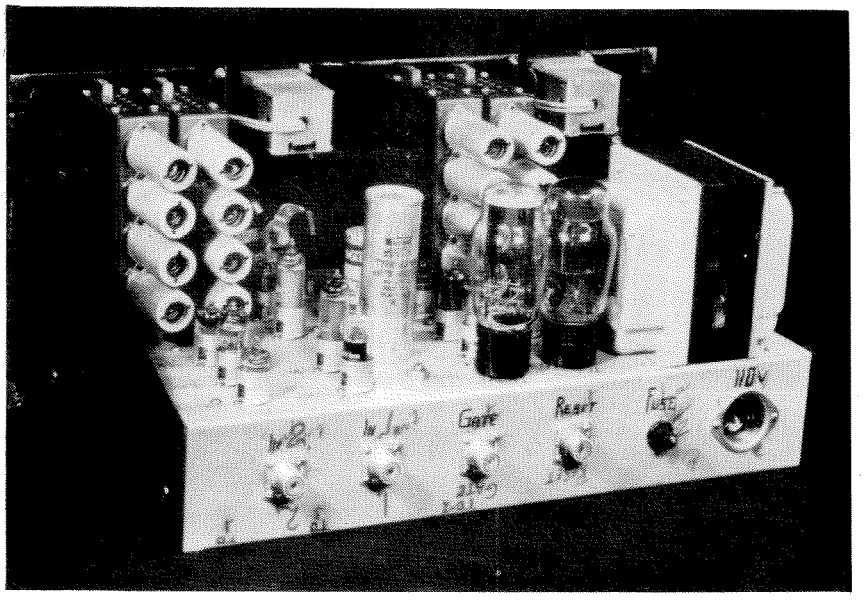

Fig. 9. Rear view of the Synchrotron Model 2 Double Scaler.

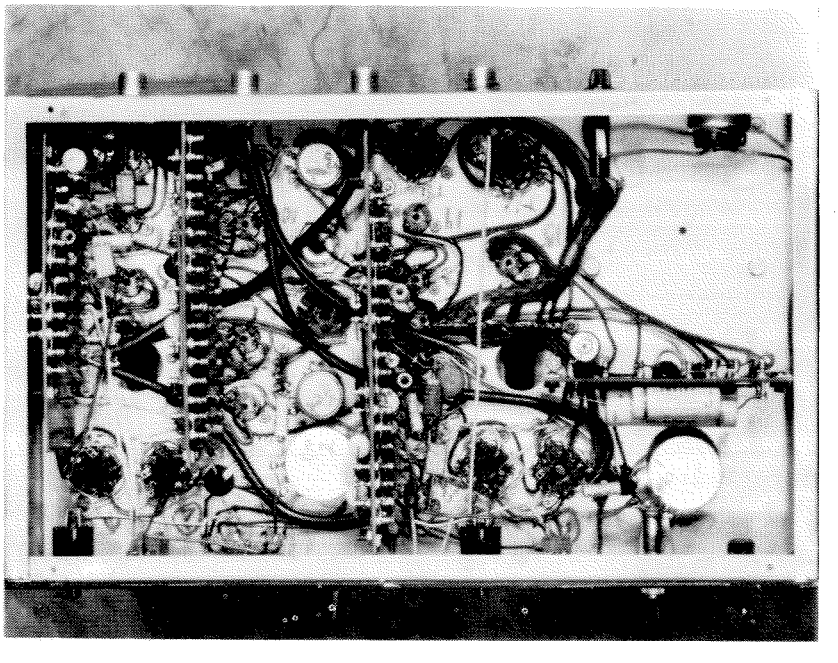

Fig. 10. Bottom view of the double scaler.

Summary and Conclusions

A large number of the components of the instrument have already been completed, but with the exception of the vacuum system, virtually all of these are yet to be tested. Some changes that will be necessary have already become apparent and undoubtedly others will appear as the electron lens and cathode assembly are tested. It remains to be seen whether the field emission cathode will give a sufficiently stable probe for convenient, rapid observations with the instrument. If it should become necessary to use a hot cathode, the estimates of per cent completion of the project will need to be revised.

The project is approximately 25% toward its completion at the time of writing this report. No scientific conclusions are possible at this time.

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